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Acid episodes in the Allt a'Mharcaidh, Scotland: an investigation based on sub-hourly monitoring data and climatic patterns

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Abstract

Stream waters in the Allt a'Mharcaidh catchment (Cairngorms, Scotland) have been monitored for flow, conductivity and pH at sub-hourly resolution; and for a range of chemical, biological and physical parameters, less intensively, since the mid-1980s. The Allt a'Mharcaidh stream is subject to acidic events (pH<5.5) triggered by both hydrology and sea-salt inputs from the atmosphere. This paper investigates the drivers of these acidic events using variables derived from sub-hourly monitored data. It also examines the influence of the North Atlantic Oscillation (NAO) on episode severity. Sub-hourly datasets are used to derive multiple regression models expressing stream H^+ concentration as a function of the sea-salt conductivity and the peak instantaneous flow rate amongst other explanatory variables. The relationship between sea-salt conductivity and the NAO is significant but hidden due to issues such as time lags and the influence of atmospheric patterns other than the NAO.

Keywords: acidic episodes, stream, sub-hourly monitoring, sea-salt conductivity, Antecedent Runoff Index, North Atlantic Oscillation, UKAWMN, Mharcaidh

Introduction

Acidic pollutant deposition can affect stream water quality when the catchment has insufficient acid neutralising capacity (ANC) to counterbalance the acidification effect (Rush, 2000). Thus, in sensitive upland ecosystems, which make up much of the UK upland areas, loadings of acid deposition can lead to acidic episodes in the stream water, with subsequent aquatic ecosystem damage (Schreiber, 1995). An acidic event can cause ecological harm when the pH < 5.5 (Harriman *et al*., 1990).

Over the last 15 years, legislative measures to reduce atmospheric emissions have proved beneficial in many cases: where severely affected sites used to experience chronic acidification, low pH is now observed less frequently. Even so, the biota can still be affected severely during short-term periods of acute acidification, thus underlining the importance of studies on episodic acidification (Ormerod *et al*., 1987).

The acidity of streams can be influenced not only by the acidity of the incoming rainfall (indeed, much of this acidity is strongly attenuated within the catchment), but also by factors such as sea-salt deposition, organic acid inputs and nitrate or sulphate pulses (Evans *et al*., 2005). The UK, a maritime country, experiences salt-laden rain from North Atlantic frontal weather systems. Sea-salt induced acidification (Langan, 1989) occurs due to cation exchange processes within the acidic soils; in acid soils, the exchanged cations will be mainly the acid cations H^+ and Al^{3+} (Evans *et al*., 2001). The sea-salt effect decreases soil acidity, but increases the acidity of percolating solutions, thus leading to the short-term acidification of the runoff (Heath *et al*., 1992).

The North Atlantic Oscillation or NAO is the most prominent and recurrent atmospheric pattern over the middle and high latitudes of the Northern Hemisphere in winter and spring (Hurrell *et al*., 2003). The NAO refers to a large-scale fluctuation in atmospheric pressure between the subtropical high pressure system near the Azores in the Atlantic Ocean and the sub-polar low pressure system near Iceland. The NAO is quantified by the NAO Index (NAOI); a positive NAOI implies very low pressures over Iceland and strong high pressures over the subtropical Atlantic.

During a positive NAOI, westerly air masses are enhanced and move across northern Europe, bringing relatively warm and moist maritime air, while stronger northerly winds carry cold air over Greenland and north-eastern Canada. Hence, a season-long positive NAOI results in warmer and wetter winters in Europe and colder and drier winters in northern Canada and Greenland. A negative NAOI indicates weak systems of low pressure over Iceland and high pressure over the subtropical Atlantic, resulting in dry, cold winters in northern Europe. Westerlies, recognised by a positive NAOI, carry airborne sea-salt from the ocean; as the winds move overland, sea-salt is deposited and the stronger the Westerlies, the greater the amount of sea-salt dropped.

To quantify the sea-salt as well as other types of acidification event, the dynamics of stream water quality changes have to be monitored on an event-by-event basis. Stream hydrochemical response to acid deposition in sensitive upland catchments has been studied extensively using periodic (e.g. monthly or weekly) spot-sampled data but, much less commonly, using sub-hourly monitoring. Nonetheless, the dynamics of acid episodes can be characterised fully only by sub-hourly monitoring. Yet, although sub-hourly datasets have determined characteristics such as alkalinity (Jarvie *et al*., 2001) or electrical conductivity (Robson *et al*., 1992) and also show time-series of pH, little use has been made of the data to estimate, systematically, acidic episode type and severity.

In this paper, sub-hourly data are examined for a major UK study of upland acidification in the Allt a'Mharcaidh catchment in the Cairngorm area of Scotland. This study, undertaken originally as part of the Royal Society's Surface Water Acidification Programme (SWAP; Mason, 1990) was, later, part of the United Kingdom Acid Waters Monitoring Network Programme (UKAWMN; Monteith and Evans, 2000). This transitional catchment is also one of the two UK sites in the UNECE Integrated Monitoring Programme (UNECE-IMP; Kleemola and Forsius, 2003), thus underlining the relevance of the study at the Allt a'Mharcaidh site, not only at a national but also at an international level. The issues addressed in this paper are:

> Is it possible to identify the drivers that control the acidic episode severity, using variables derived from sub-hourly monitored data?
>
> How might large scale atmospheric patterns, such as the North Atlantic Oscillation, influence the drivers of acidic episode and, thus, acidic episode severity in the future?

This work is a key component of the Euro-limpacs project, aimed at assessing the effects of future global change on Europe's freshwater ecosystems (http://www.eurolimpacs.ucl.ac.uk/).

Background information

SITE DESCRIPTION AND DATA COLLECTION

The Allt a'Mharcaidh catchment is a steep-sided 9.98 km^2 moorland catchment in the Cairngorm Mountains, Eastern Scotland (Fig. 1) (Ferrier *et al*., 1990). It has a maximum elevation of 1111 m, comprises biotite-granite overlain by alpine and peaty podzol soils or peat and receives on average over 1300 mm of rain per annum. The stream is well-buffered (mean pH 6.45) yet susceptible to acid episodes of pH below 5.5 (Monteith and Evans, 2000). The Allt a'Mharcaidh has been monitored since the mid-1980s (Monteith and Evans, 2000). This catchment is part of the United Kingdom Acid Waters Monitoring Network (UKAWMN), for which physical, chemical and biological monitoring has been undertaken at different time-steps (e.g. monthly, weekly, sub-hourly). Among other variables, flow, electrical conductivity (EC), temperature and pH have been measured at sub-hourly resolution at the stream outfall. An automatic weather station at 610 m in the centre of the catchment recorded hourly meteorological data. More details on sampling and analytical procedures in the Allt a'Mharcaidh catchment can be found in Patrick *et al*. (1991).

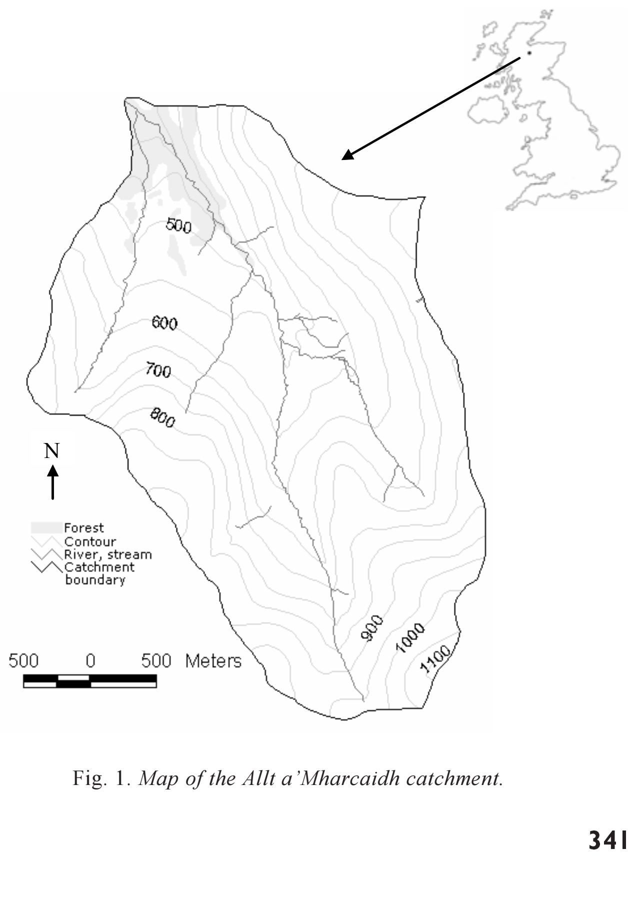

Fig. 1. *Map of the Allt a'Mharcaidh catchment.*

Rainfall chemistry data were obtained from the UK National Air Quality Information Archive (AEAT) for the Allt a'Mharcaidh. Chloride concentration in precipitation was measured on weekly bulk- collection samples (Clark, 1998).

CHARACTERISATION OF ACIDIC EPISODES

An 'episode' in the context of river water acidification and water quality dynamics generally refers to any short-term event induced by extreme, irregular physical, chemical or biological changes, which also has an ecological impact. For acid-sensitive systems, such an ecological impact may be a temporary decrease in streamwater pH that could be detrimental to the stream fauna and flora. In this paper an acidic event is a storm event during which the stream pH drops below 5.5; indeed, Harriman *et al*. (1990) indicate that a pH as high as 5.5 can challenge the survival of fish and other biota. Acid episodes can be triggered by different climate-related drivers, such as heavy rainfall or snowmelt (dilution episodes) sometimes accompanied by enhanced sea-salt deposition (sea-salt episodes). Episodes may last over several hours to days or even weeks.

According to Davies *et al*. (1992), the dilution process associated with heavy rainfall or snowmelt is the most widespread mechanism of episodic acidification in Europe. Stream pH and ANC are typically highest during low flows but may decline when a large input of rainwater or snowmelt reaches the stream directly or through mixing with pre-event water that had percolated through the soil sub-surface or surface flowpaths. The severity of dilution events depends not only on the characteristics of the rain/snowmelt but also on the catchment biogeochemical characteristics, its hydrology and its antecedent conditions (i.e. catchment wetness).

Sea-salt deposition is also an important cause of acidic episodes (Wright *et al*., 1988). When sea-salt-rich precipitation is deposited (either wet or dry), a significant fraction of the incoming cations Na^+ and Mg^{2+} is exchanged for other cations in the soils. In acid soils, the exchanged cations will be mainly the acid cations H^+ and Al^{3+}. This natural process of cation displacement is called the 'sea-salt' effect; it decreases soil acidity but increases the acidity of percolating solutions, thus leading to short-term acidification of the runoff and a reduction in pH and ANC. As with dilution events, the catchment chemical and hydrological characteristics as well as its antecedent conditions influence the severity of the 'sea-salt driven' episodes.

While the flow in a watercourse reflects the incoming rainfall, it also depends strongly on the antecedent catchment conditions, particularly the catchment moisture status, which has a strong influence on the runoff and consequently on the severity of acidic episodes in the stream. As a measure of the catchment wetness, an Antecedent Runoff Index (ARI) may be determined. The ARI is analogous to the Antecedent Precipitation Index in Heggen (2001), but it involves runoff rather than rainfall and so is more indicative of the wetness of the catchment. The ARI is calculated as:

$$ARI = \sum_{i=1}^{\infty}[k^{i-1} * R_{(t-i)}] \tag{1}$$

where i is the number of 24 hour periods prior to storm onset, t is the time of storm onset, R is the total runoff in the 24 hour period and k is a parameter determining memory length ($0<k<1$).

Several values for the coefficient k were assessed in this paper. As k increases towards a value of 1, the influence of long-term past conditions becomes more important. For example, for k=0.8, the runoff that occurred three weeks ago still affects the ARI value while with k=0.5, the rainfall that occurred only one week ago has little influence. ARI for one week and ARI for three weeks are thus defined and have been determined for each time step of the sub-hourly monitored runoff data. The time of storm onset was the time-step immediately prior to the rising limb of the hydrograph. The ARI may also reflect catchment chemical dynamics. While wet organic soils can accumulate non-marine sulphur, on drying (i.e. ARI is low), oxidation can lead to acidifying flushes of sulphate in subsequent events (Huntington *et al*., 1994).

pH is a measure of acidic episode severity. The pH or H^+ concentration in a stream during a storm event may be influenced by factors such as the storm peak flow rate, the sea-salt conductivity, the antecedent catchment conditions and the stream temperature.

DERIVATION OF SEA-SALT CONDUCTIVITY DATA

Corrections of pH and EC data

The data for sub-hourly monitored flow, pH and electrical conductivity (EC) were most complete for the period between 01/01/1991 and 31/12/1994. To check the quality of this dataset, manual spot sample data were compared with the data monitored at a frequency of 20 minutes. For flow, no correction was needed. However, for pH, there were discrepancies that increased in time between the sub-hourly and the manual spot sampled data; sub-hourly measurements were consistently lower than the spot sampled data and so underestimated the true pH.

Davison and Woof (1985) attribute the difficulties associated with pH measurements at low dissolved solids content as being due to systematic errors because of insufficient flux through the electrode junction of the internal solution. Moreover, the performance of aging probes may drift over time (Evans *et al.*, 2005). Likewise, for EC, discrepancies were also observed. Sub-hourly measurements were consistently lower than spot sampled data, perhaps due to a calibration error. The correction of sub-hourly pH and EC data is, therefore, required and is described in Robson (1993). Although subsequent analysis is concerned primarily with the period November 1990 to December 1994, the pH and EC records are good for the whole of 1990 and, hence, these data are also used in the correction. The equation for the correction of the sub-hourly pH data, based on linear regression, is:

$$pH_{corrected} = 0.875 + 0.899\,pH_{rawdata} + 0.003t \quad (R^2 = 0.84,\ n=42 \text{ and } p<<0.001) \qquad (2)$$

where *t* is the time elapsed since the start of 1990 (in hours).

The correction equation for the EC ($\mu S\ cm^{-1}$) is:

$$EC_{corrected} = 0.939EC_{rawdata} + 4.905 \quad (R^2 = 0.89,\ n= 40 \text{ and } p << 0.001) \qquad (3)$$

Both correction equations for pH and EC were applied to the sub-hourly datasets. From this point onwards, the terms 'sub-hourly pH' and 'sub-hourly EC' refer to the corrected pH values and the corrected EC values respectively.

Sea-salt conductivity data determination

In upland catchments, ions derived from atmospheric sources (such as sea-salt or industrial emissions) constitute an important component of the stream water EC (Jarvie *et al.*, 2001). The Allt a' Mharcaidh catchment is far from any major urban industrial areas and, thus, it might be assumed that pollutants would not contribute significantly to the EC of the stream water. However, at the Allt a'Mharcaidh, anthropogenic pollutants, such as the non-marine sulphate, account for about 19% of the total dissolved solids (determined through the charge ratio, in $\mu eq\ L^{-1}$, between anthropogenic pollutant with counterbalancing cations and total major anions and cations). By comparison, at a more polluted site like the River Etherow in England (Monteith and Evans, 2000), the contribution of total pollutants to the total dissolved solids in the stream is about 44%.

To assess the sea-salt variation in the streams using the EC data, other influences on the EC have to be factored out. The total electrical conductivity (C_T) consists largely of two terms: the sea-salt component of EC (C_{SS}) and the non sea-salt component of EC (C_{NSS}). The latter subdivides into two parts, C_W, associated with carbon dioxide-induced weathering of base cations from the soils and bedrock that lead to the formation of calcium and magnesium bicarbonate-bearing waters (sometimes enriched with two additional base cations, sodium and potassium) and C_A, associated with the acidification process and the generation of hydrogen and aluminium ions. Thus,

$$C_T = C_{SS} + C_{NSS} = C_{SS} + C_W + C_A \qquad (4)$$

Of these terms, the EC associated with the weathering sources, C_W, will be correlated directly with the bicarbonate concentration (except under highly alkaline conditions not appertaining here, when carbonate anions become important) and will be approximately inversely proportional to 10^{-pH}. This is because the bicarbonate concentration is approximately inversely related to the hydrogen ion concentration for a constant carbon dioxide pressure (Neal *et al.*, 1998a; Neal *et al.*, 1998b) and so the equivalents of base cations associated with the bicarbonate generation will equal the bicarbonate concentration in equivalents. Correspondingly, the acidity components of the EC, C_A, will be approximately proportional to the hydrogen ion concentration and thus C_A will be approximately proportional to 10^{-pH}.

Spot sample data for HCO_3^-, Cl^- were used with spot sample pH data to express the non sea-salt contribution of the total EC (i.e. $C_W + C_A$). This is done through a step-by-step process. Assuming that chloride is entirely marine-derived and that it is unreactive within the catchment, initially, the stream sea-salt conductivity, C_{SS}, was assessed using chloride ions as a surrogate for sea-salts. Thus, the sea-salt conductivity associated with the chloride stream concentration was calculated using the ratio between seawater conductivity and the Cl^- concentration in seawater (19 000 mg L^{-1}) for each monthly spot sample measurement. Then, the non sea-salt component of the EC (i.e. C_{NSS}) was calculated as the difference between the spot sample EC and the previously calculated spot sample sea-salt conductivity. Then, the alkalinity was used in conjunction with the pH to estimate the bicarbonate concentration. C_{NSS} (i.e. $C_W + C_A$) was then regressed against the hydrogen ion concentration (in $\mu eq\ L^{-1}$) and the bicarbonate concentration (in $\mu eq\ L^{-1}$) to give:

$$C_w + C_A = 8.641 + 0.501 * H^+ + 0.096 * HCO_3^- \quad (R^2=0.37,\ n=37 \text{ and } p < 0.0005) \qquad (5)$$

To express the non-sea-salt conductivity as a function of pH and EC (as needed for use with the sub-hourly data), the bicarbonate concentration (in $\mu eq\ L^{-1}$) was regressed against the pH, giving:

$$HCO_3^- = 1.514 * 10^{-3} * 10^{0.681pH}$$
(R^2=0.91, n=37 and p < 0.0005) (6)

Introducing Eqn. 6, expressing the bicarbonate concentration as a function of pH, into Eqn. 5, gives:

$$C_w + C_A = 8.641 + 5.010 * 10^5 * 10^{-pH} + 1.453 * 10^{-4} * 10^{0.681*pH} \quad (7)$$

The equation is similar to that derived by Robson (1993) and more complex than the one derived by Jarvie *et al.* (2001) where there was not the same need to include the C_A term as the pH was higher. Equation 7 was then applied to the sub-hourly EC dataset, and the sea-salt conductivity for each time step was calculated using Eqn. 4.

NORTH ATLANTIC OSCILLATION INDEX (NAOI)

The traditional measure of the North Atlantic Oscillation is the difference of the normalised sea level pressure anomaly between Iceland and the subtropical eastern North Atlantic (Portis *et al*., 2001). Although seasonal or monthly mean NAOI are commonly used, standardised daily NAOI values in this study are based on meteorological re-analyses of data from the National Centre for Environmental Prediction (NCEP; Hindar *et al*., 2004). More details on how this daily NAOI is defined can be found in Orsolini and Limpasuvan (2001). As the NAOI presents high positive values in winter, thus underlining strong Westerlies, only the daily NAOI for the winter months (November to April included) from 1990 to 1994 were considered here.

Identification of acidic episodes and their drivers

Lynch *et al*. (1986) evaluated the changes in stream water chemistry due to storm events using hourly and weekly data for hydrological and pH variables. This paper extends this analysis by using sub-hourly data, not only for hydrological variables and pH but also for sea-salt conductivity and stream temperature, to investigate the controls on episode severity (such as minimum stream pH or maximum stream H^+ concentration).

Considering the 1991–94 Allt a'Mharcaidh sub-hourly corrected pH and EC dataset, many acidic episodes (pH<5.5 during a storm event) were identified and the auto-correlation of the pH data was assessed. This revealed that a period of a month is necessary to ensure that selected episodes are independent of each other (Fig. 2); after this screening 17 (independent) episodes were evaluated further.

The maximum hydrogen ion concentration (μeq L^{-1}) for each of the 17 episodes was chosen as an indicator of an acute aspect of acidification. The independent variables (defined in Fig. 3) considered when trying to quantify the severity of acidic episodes (i.e. the maximum H^+ concentration) were:

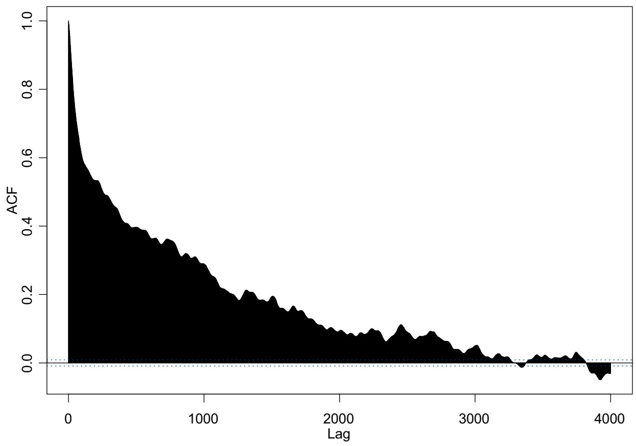

Fig. 2. *Autocorrelation plot: pH data from January 91–October 92 at the Allt a'Mharcaidh (data representative of the whole study period of November 1990-December 1994). ACF = autocorrelation function and lag = lag in 20 minute time steps.*

Maximum sea-salt conductivity (μS cm^{-1});
Peak instantaneous flow rate (m^3 s^{-1});
Three-week ARI (taken for the start of the first flow event within an episode);
Mean stream temperature (°C, mean of the temperature data recorded during the episode);
One-week ARI (determined as for the three-week ARI);
Minimum sea-salt conductivity (μS cm^{-1});
Episode duration (hours);
Range of sea-salt conductivity (μS cm^{-1}).

Table 1 shows the range taken by each of these variables.

Sea-salt inputs, reflected in the sea-salt conductivity, and the air temperature, reflected by the mean stream temperature, are climate-related factors that influence the stream pH. The former can be responsible for temporary increases in concentrations of H^+ and Al^{3+} in runoff after exchange with 'sea-salt cations' (Na^+ and Mg^{2+}). The latter provides an indication of snow-melt and rainfall.

Analysis of twice weekly spot sampled data from the Allt a'Mharcaidh catchment indicated that 75% of the variability in pH and alkalinity can be explained by flow (Harriman *et al*., 1990). Indeed, when focusing on responses at high flow, Harriman *et al*. (1990) found that the higher the flow, the higher the contribution of dilute, event-related, poorly-buffered surface water, and the lower the contribution of

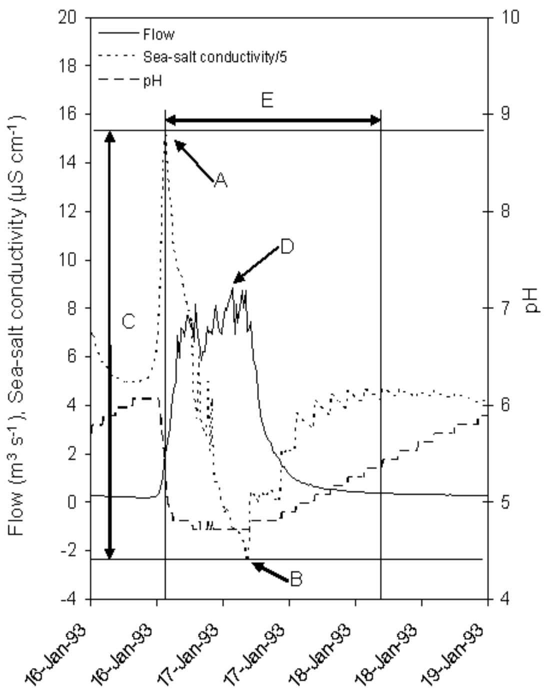

Fig. 3. *Acid episode of the 16–18 of January 1993 (43 hours duration), presenting some of the independent variables taken in the multiple regressions: sea-salt conductivity variables (A: maximum, B: minimum and C: range of sea-salt conductivity), D: peak instantaneous flow rate, E: episode duration (hours).*

sub-surface water. The antecedent catchment conditions, as reflected by the ARI variables, have an influence on the quantity of rainfall reaching the stream and, therefore, on the change in stream flow and thus on pH. The episode duration, defined as the period between the beginning of the event (i.e. when the pH drops below 5.5) and the end of the event (i.e. when the pH again rises to 5.5) is also taken into consideration.

To evaluate the best independent variables to include in the model to predict the maximum H^+ concentration, a stepwise multiple regression was used; it allows the use of automated processes in a search for the best model by adding independent variables to and deleting independent variables from the model until no further changes are appropriate (Lynch *et al.*, 1986). This approach provides a multiple regression equation with a coefficient of determination (R^2) as close to 1 as possible and with the minimum number of independent variables. The stepwise selection also takes the C_p criterion into account when choosing the best model. C_p represents the total squared error of *n* fitted observations of the dependent variable (Y) for a given regression function and optimally, a C_p close to the number of independent variables included in the model is representative of a descriptive model regression (Lynch *et al.*, 1986).

The analysis of the selected 17 storm events (Table 2) shows that even though hydrology, as represented by the flow variable, is clearly important in determining the maximum episodic H^+ concentration (correlation coefficient = 0.59, for the peak instantaneous flow rate, Table 2), the sea-salt conductivity terms, despite the inland location of the site, can account for most of the variability in the maximum H^+ concentration (correlation coefficient = 0.80 for the maximum sea-salt conductivity and the range of sea-salt conductivity, Table 2). Although the sea-salt conductivity was calculated using the H^+ concentrations, it is believed that H^+ has a minimal influence on the variation of the sea-salt conductivity variable on a storm event time-scale. Indeed, Fig. 4 shows that the sea-salt conductivity represents about 50% of the total conductivity and follows the same fluctuations as the total conductivity variable. The effect of stream temperature appears to have little impact on the episodic pH response. The ARI variables were found to have no significant influence on episode severity. The pre-storm antecedent conditions also influence the catchment hydrological response. The episode duration has a good correlation with the maximum H^+ concentration (correlation coefficient = 0.69, Table 2).

The information contained in Table 2 was used to assess the impact of including or removing specific variables in the multiple regression models. The performance of the

Table 1. Variations of the 17 storms independent variables considered in the multiple regression models.

	Mean	*Minimum*	*Maximum*
Maximum sea-salt conductivity (µS cm^{-1})	17	6.1	96
Peak instantaneous flow rate (m^3 sec^{-1})	4.6	1.2	1.6
Three weeks ARI	1200	450	2900
Mean stream temperature (°C)	5.0	2.0	9.5
One week ARI	590	190	1500
Minimum sea-salt conductivity (µS cm^{-1})	9.5	2.4	29
Episode duration (hours duration of pH<5.5)	15	1.3	62
Range of sea-salt conductivity (µS cm^{-1})	7.7	0.9	66

Table 2. Correlation coefficients (R) between the different variables. Values with $p<0.01$ are given in bold and underlined for $p<0.05$ ($n = 17$).

	Maximum H^+ (μeq L^{-1})	*Maximum sea-salt conductivity (μS cm^{-1})*	*Peak instantaneous flow rate (m^3 sec^{-1})*	*Three weeks ARI*	*Mean stream temperature (^oC)*	*One week ARI*	*Minimum sea-salt conductivity (μS cm^{-1})*	*Episode duration (hours duration of pH<5.5)*	*Range of sea-salt conductivity (μS cm^{-1})*
Maximum H^+ (μeq L^{-1})	1								
Maximum sea-salt conductivity (μS cm^{-1})	**0.80**	1							
Peak instantaneous flow rate (m^3 sec^{-1})	0.59	0.36	1						
Three weeks ARI	–0.07	0.06	0.19	1					
Mean stream temperature (^oC)	–0.21	–0.32	–0.13	–0.55	1				
One week ARI	0.04	0.13	0.29	**0.93**	–0.48	1			
Minimum sea-salt conductivity (μS cm^{-1})	**0.65**	**0.87**	0.08	–0.27	–0.14	–0.27	1		
Episode duration (hours duration of pH<5.5)	**0.69**	*0.57*	0.41	0.05	–0.42	0.23	0.37	1	
Range of sea-salt conductivity (μS cm^{-1})	**0.80**	**0.98**	0.44	0.19	–0.36	0.28	**0.75**	**0.61**	1

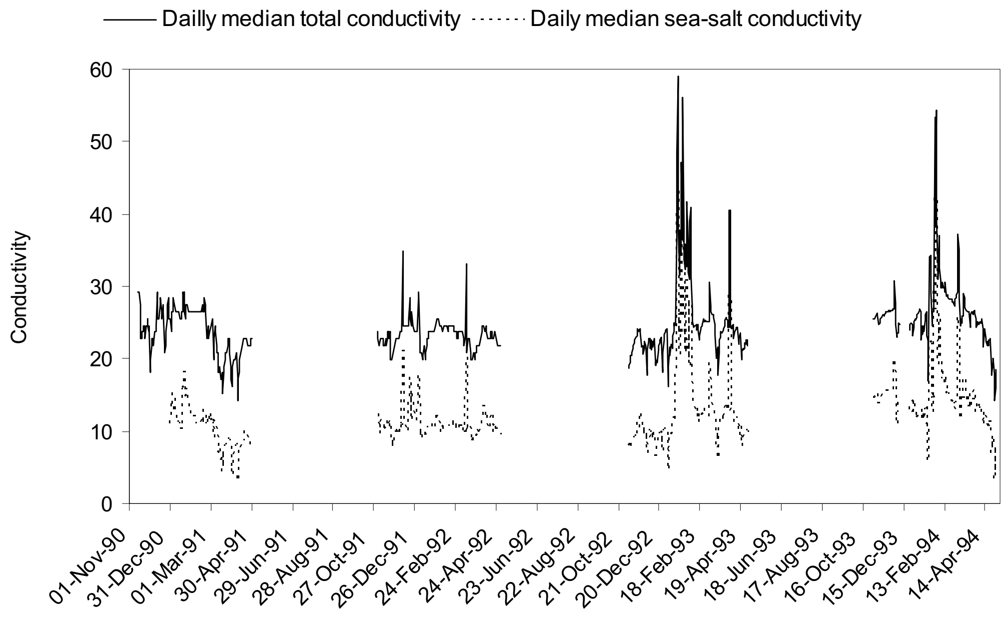

Fig. 4. *Time-series plot of the daily median total conductivity (μS cm^{-1}) and the daily median sea-salt conductivity (μS cm^{-1}) for the four winter periods (11/90–04/91, 11/91–04/92, 11/92–04/93, 11/93–04/94).*

Table 3. Options for the multiple regression models, using the maximum H^+ concentration (µeq L^{-1}) as dependent variable (F stat represents the significance of the multiple regressions).

	Model 1			*Model 2*			*Model 3*			*Model 4*			*Model 5*		
	Coeffs	*Standard Error (SE)*	*P-value*	*Coeffs*	*SE*	*P-value*	*Coeffs*	*SE*	*P-value*	*Coeffs*	*SE*	*P-value*	*Coeffs*	*SE*	*P-value*
Intercept	2.94	0.92	6.21E-03	4.16	1.26	5.81E-03	5.97	1.30	6.25E-04	2.66	0.88	9.94E-03	3.87	1.26	1.07E-02
Maximum sea-salt conductivity (µS cm^{-1})	0.14	0.03	3.57E-04	0.14	0.03	3.46E-04				0.11	0.03	4.19E-03	0.11	0.03	5.83E-03
Peak instantaneous flow rate (m^3 sec^{-1})	0.38	0.16	3.20E-02	0.42	0.16	1.97E-02	0.36	0.17	5.83E-02	0.31	0.16	6.74E-02	0.35	0.16	5.43E-02
3 weeks ARI				-0.11	0.08	1.98E-01	-0.16	0.09	8.55E-02				-0.11	0.08	2.14E-01
Episode duration (hours duration of pH<5.5)										0.07	0.04	1.25E-01	0.07	0.04	1.39E-01
Range of sea-salt conductivity (µS cm^{-1})							0.19	0.04	5.78E-04						
r^2	0.74			0.78			0.77			0.79			0.82		
F stat	7.24E-05			1.65E-04			3.48E-04			1.16E-04			5.04E-04		

models presented in Table 3 was assessed based on the highest R^2 and the highest significance of an F-ratio test. The best two-variable model uses the maximum sea-salt conductivity and the peak instantaneous flow rate as independent variables (Model 1). The best three-variable models are those involving sea-salt conductivity variables (either the maximum sea-salt conductivity or the range of sea-salt conductivity), the peak instantaneous flow rate, the three-week ARI and the episode duration (Model 2, Model 3 and Model 4). Model 3 presents a lower R^2 and higher F-Stat value than Model 2 and Model 4 presents a higher R^2 and a lower F-Stat value than Model 2. The best four-variable model is found to be Model 5, involving the maximum sea-salt conductivity, the peak instantaneous flow rate, the three-week ARI and the episode duration. Model 4 (three-variable model) is therefore the best model for estimating the maximum H^+ concentration, as selected by the automated routine, having only three independent variables: the maximum sea-salt conductivity ($\mu S\ cm^{-1}$), the peak instantaneous flow rate ($m^3\ s^{-1}$) and the episode duration (hours).

To illustrate the performance of the multiple regression models (Model 2 and Model 4) the values obtained with these models for the minimum pH of the 17 selected storms were plotted (Fig. 5) against the observed minimum pH values.

In these multiple regression analyses, the ARI has proved to be of subsidiary value only in explaining episode severity. The ARI has been found not to be significant on its own, when related to maximum H^+ concentration. This may suggest that acidifying sulphate flushes are not important features of acidic episodes at the Mharcaidh. This is possibly because episodes following summer droughts, when such phenomena are most apparent, are rare in the catchment, or were not strongly represented in the sample of storms analysed in this study. Alternatively, the catchment runoff is not strongly acidic and the buffering capacity of the soils may be sufficient to avoid sulphate pulses causing a significant decrease in episodic stream pH. Episode duration is also chosen as an independent variable, which may represent a more suitable quantifier of catchment wetness in the context of simulating episode severity. Events following dry conditions are likely to be shorter lived than those following wet conditions.

This study underlines the importance of including the sea-salt variable as well as hydrometeorological variables in characterising episodes.

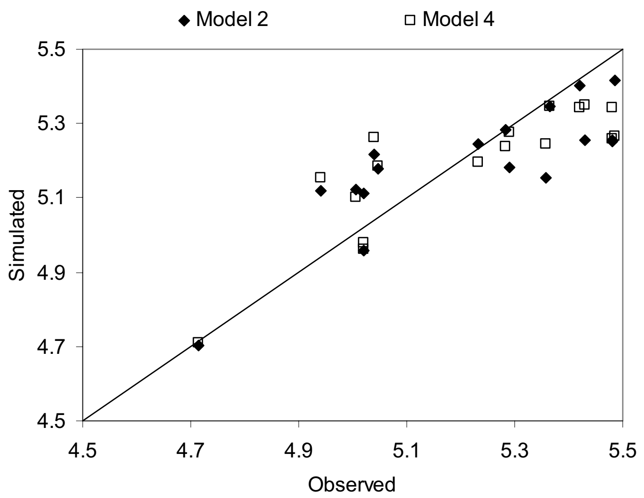

Fig. 5. *Minimum pH of selected storms (91–94): simulated against observed data for two multiple regression models (Model 2 and Model 4, as defined in Table 3).*

Acidic episodes, sea-salt and the North Atlantic Oscillation Index

The NAO has a strong influence on winter precipitation in Western Europe (Kiely, 1999) and the NAOI can be linked to sea-salt episodes in the UK and in Scandinavia (Evans *et al*., 2001; Hindar *et al*., 2004). Over recent years, the NAOI has tended towards a more positive phase and it is expected to continue to increase over the next 100 years (Ness *et al*., 2004). By exploring relationships between sub-hourly monitored data at the Allt a'Mharcaidh and the NAOI, insights can be gained on the likely dynamics of acidic episodes in the future.

When trying to link the episodic data with climate variations such as the North Atlantic Oscillation, a monthly NAOI is often used. In this study, as sub-hourly monitoring data were to be compared with the NAOI, the use of NAOI data with a smaller time-scale resolution (i.e. daily) was justified. Moreover, using daily values of the NAOI allows some relationships to arise that might be missed when using monthly values. An NAOI that would reflect the antecedent NAOI for the past three weeks or even the previous week could be used as well (as was done previously for the ARI) but is beyond the scope of this study.

Figure 6 plots the daily NAOI data along with the sub-hourly estimated sea-salt conductivity for the four successive winter periods (11/90–04/91, 11/91–04/92, 11/92–04/93 and 11/93–04/94). Inspection of the time-series allows assessment of the factors influencing the sea-salt conductivity. A sea-salt conductivity baseline of approximately 12 $\mu S\ cm^{-1}$ is observed, while peaks in sea-salt conductivity are usually storm-related and often are preceded by a high NAOI (e.g. 19/12/91, 23/12/91, 23/11/92, 05/03/94, Fig. 7). However, some episodes show sea-salt conductivity troughs during times of high NAOI (e.g. 02/12/92, Fig. 8), where the high flow, abundant rainfall

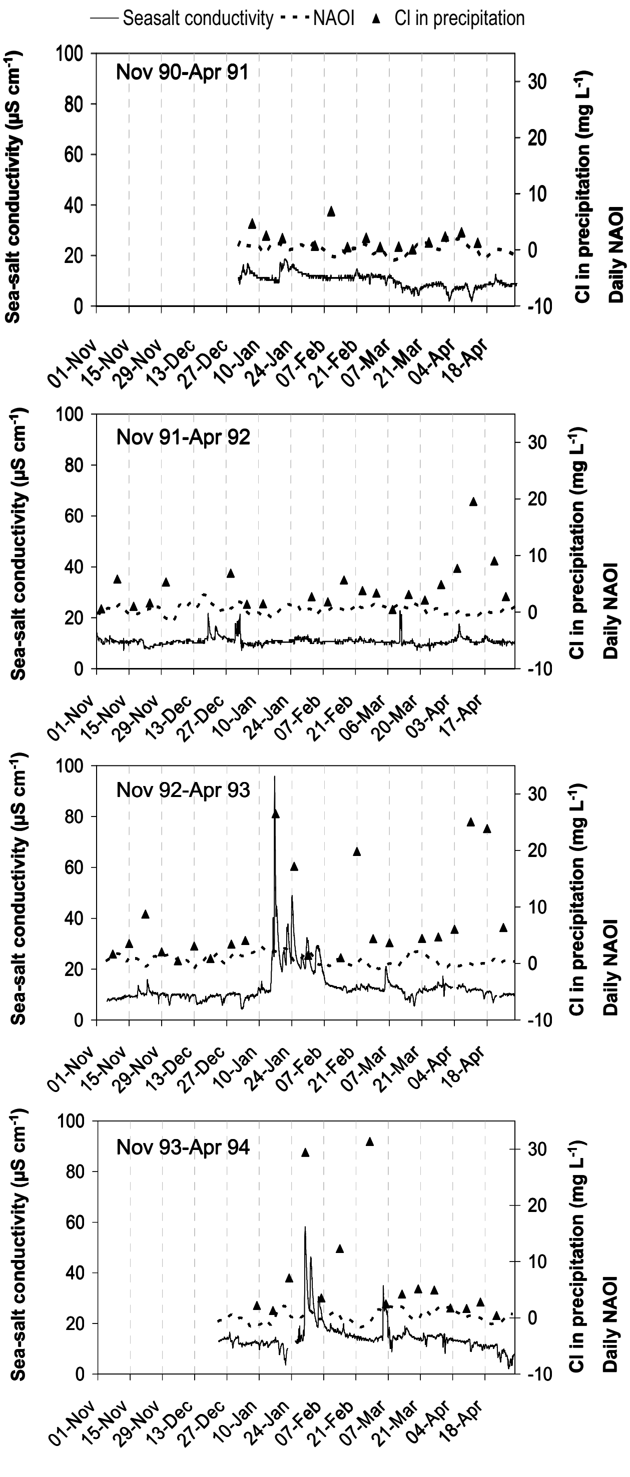

Fig. 6. *Time series plots of sea-salt conductivity (µS cm⁻¹), daily NAOI, Cl in precipitation (mg L⁻¹) at the Allt a'Mharcaidh, for 4 successive winters (11/90-04/91, 11/91–04/92, 11/92–04/93 and 11/93–04/94).*

and drop in pH suggest acidic episodes due to dilution. In spring '94 (Fig. 6) a progressive decline in sea-salt conductivity is associated with decreasing NAOI and a sequence of dilution events. More complex responses are also apparent. Some storms show sea-salt conductivity troughs of dilution preceded by sea-salt conductivity peaks (e.g. 01/01/92, Fig. 6). To explain this phenomenon, weekly data of Cl^- in rainfall were plotted alongside the NAOI and sea-salt EC records. Figure 8 shows that conditions of very high Cl^- in rainfall and prolonged high NAOI yield to (i) the highest sea-salt conductivity in storms, and (ii) elevated sea-salt conductivity in baseflow (e.g. January 93).

The Cairngorm Mountains are renowned as the snowiest part of the UK (Helliwell *et al.*, 1998). Therefore, the influence of snow packs on acidic episodes must also be considered. Helliwell *et al.* (1998) indicate that the volume and the rate at which the snow melts clearly influence the annual flow regime and the chemistry of the Allt a'Mharcaidh. As underlined in the same study, high flows go with major acidic episodes generated by the elution of pollutants deposited on the snow or contained in the snow. The most direct link between the quality of the snow and the runoff was found to be the release of sea-salt (SO_4^{2-} and Cl^- ions). An episodic event linked with the release of sea-salts through snow melt is apparent on 20/01/1991 (Fig. 9). Analysis of the data shows that negative temperatures associated with low rainfall indicated the presence of snow on site. When the temperature rose, the concentrated sea-salt snow melted thus leading to an episodic event (high flows and drop in pH).

To assess the relationship between NAOI and sea-salt conductivity, daily median sea-salt conductivity data (derived from the sub-hourly dataset), correlated with daily NAOI, gave a value of 0.16 (n=645, p=0.001, Fig. 10). This weak relationship might be due to the fact that the NAO and the resulting observed change in stream chemistry (reflected by the sea-salt conductivity), are not coincident. Such time lags occur because the NAOI is calculated as a pressure difference distant from the location of the study site (Hindar *et al.*, 2004). Thus, time delays will occur between the measured sea level pressures in the Atlantic Ocean (basis for the index), and the resulting weather conditions, depositions and associated effects at the Allt a'Mharcaidh. Moreover, on-site meteorological and catchment processes may also delay the NAOI influence on the stream chemistry (antecedent catchment conditions, weather changes such as snow melt events, etc.). Such relationships are, however, beyond the scope of this study and, thus, are not investigated further.

To take this time delay into account, a cross-correlation analysis was performed on the daily NAOI and the daily median variables, derived from the sub-hourly monitored datasets (i.e. sea-salt conductivity, pH and flow) for the four winter periods (11/90–04/91, 11/91–04-92, 11/92–04/93 and

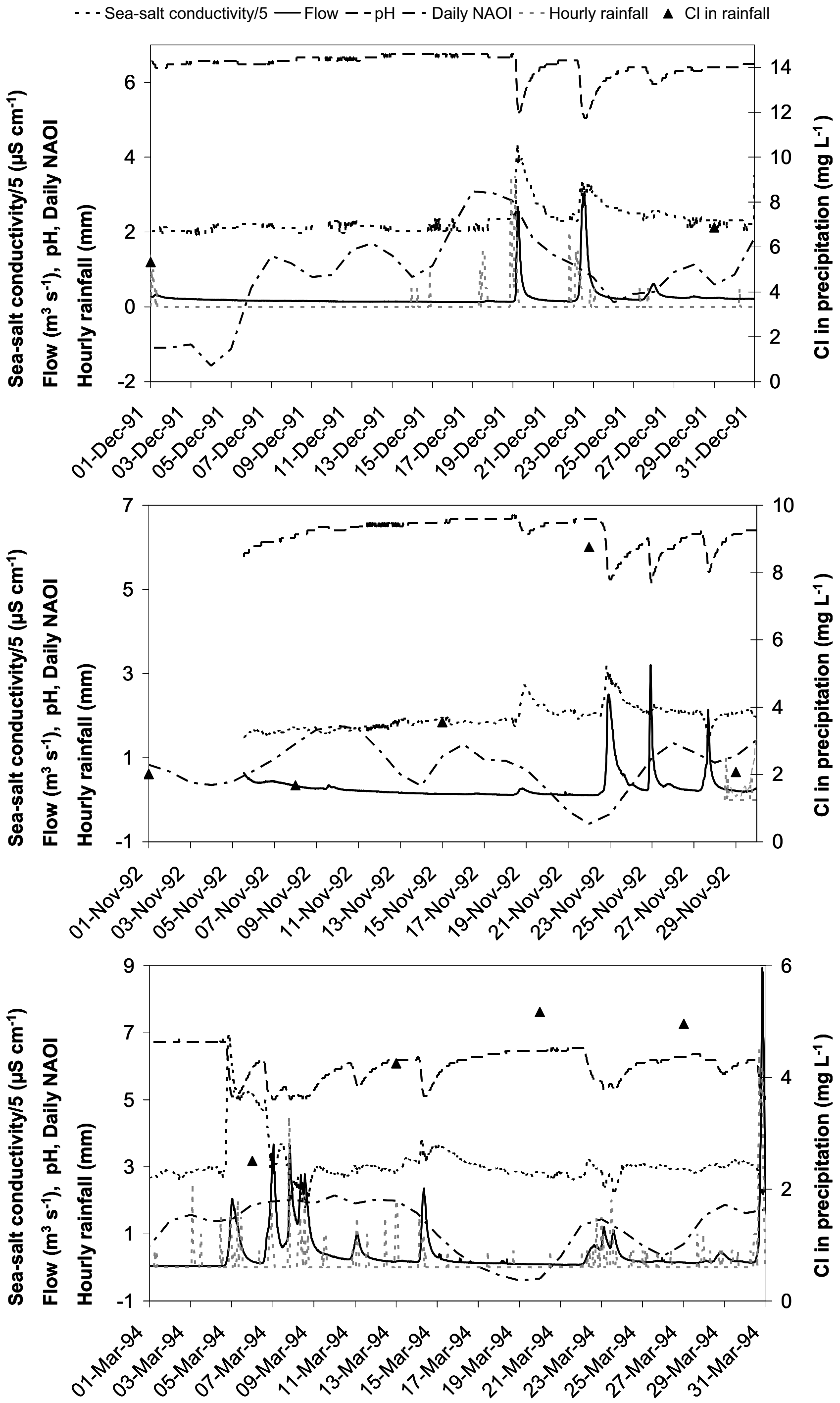

Fig. 7. *Time-series plots of sea-salt conductivity (µS cm⁻¹), flow (m³ s⁻¹), pH, daily NAOI, hour rainfall (mm), Cl in precipitation (mg L⁻¹) , for December 91, November 92 and March 94.*

11/93–04/94). In this test, the correlation between two time-varying series over time intervals that may or may not be coincident is assessed (Boker *et al*., 2002). Preliminary cross-correlation tests were run between daily median flow and daily median pH data for the four winter periods (Fig. 11). A strong significant inverse relationship between the pH and flow was observed for each of the winter periods assessed, with no time lag apparent at a daily resolution.

The cross-correlation test was then performed between the daily median sea-salt conductivity and the daily NAOI data, for each of the 4 winter periods (Fig. 11). The highest correlations between the sea-salt conductivity and the NAOI

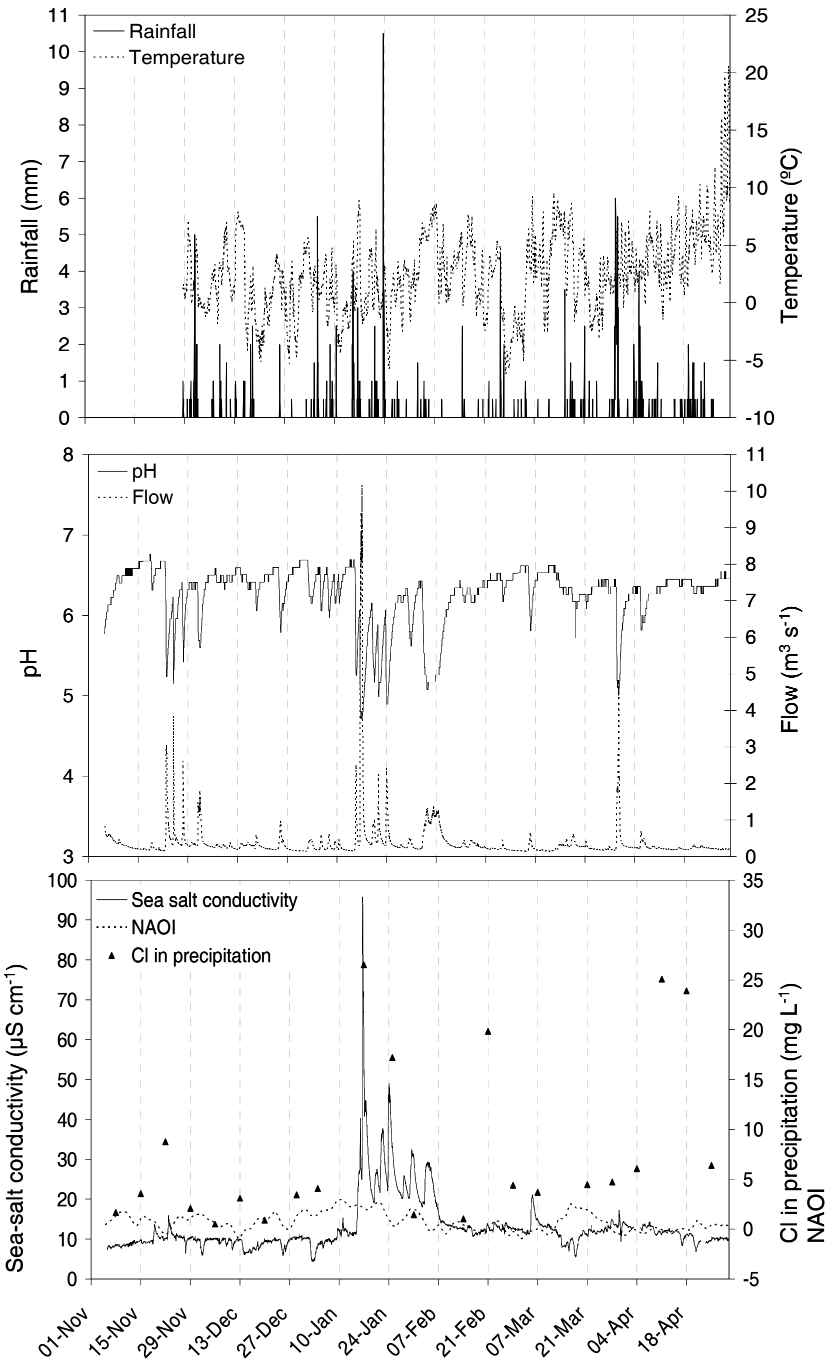

Fig. 8. *Time-series plots of sea-salt conductivity/5 ($\mu S\ cm^{-1}$), daily NAOI, Cl in precipitation ($mg\ L^{-1}$), pH, flow ($m^3\ s^{-1}$), rainfall (mm) and temperature (°C) at the Allt a'Mharcaidh for the winter 92–93 (11/92–04/93).*

data take place at lags of about 24 days for the winter 1990–91, 1 day for the winter 1991–92, and 3 days for the winter 93–94. The highest correlation between the two variables occurs during the winter 1992–93, at a lag of about 13 days. This means that during the winter 1992–93, the sea-salt conductivity observed in the stream during an acidic event was reflecting a NAO index that took place about 13 days earlier.

Figure 12 presents a time-series plot of the daily NAOI and the delayed daily median sea-salt conductivity. The peaks in sea-salt conductivity, occurring during periods of high flow, appear to match the daily NAOI. However, during sea-salt conductivity troughs (low flow) no clear relationship can be identified between the variables as there is no hydrological atmospheric–stream channel connection between the sea-salt conductivity and the NAOI. Such

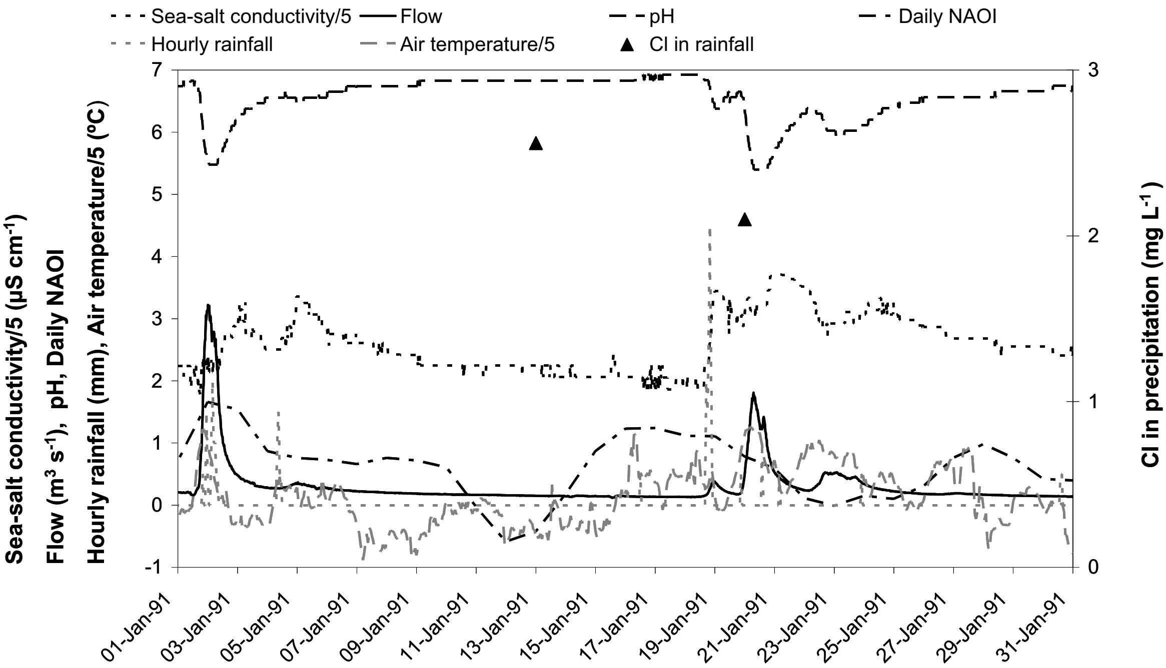

Fig. 9. *Time-series plots of sea-salt conductivity (µS cm^{-1}), flow (m^3 s^{-1}), pH, daily NAOI, hourly rainfall (mm), air temperature (°C), Cl in precipitation (mg L^{-1}), for January 91.*

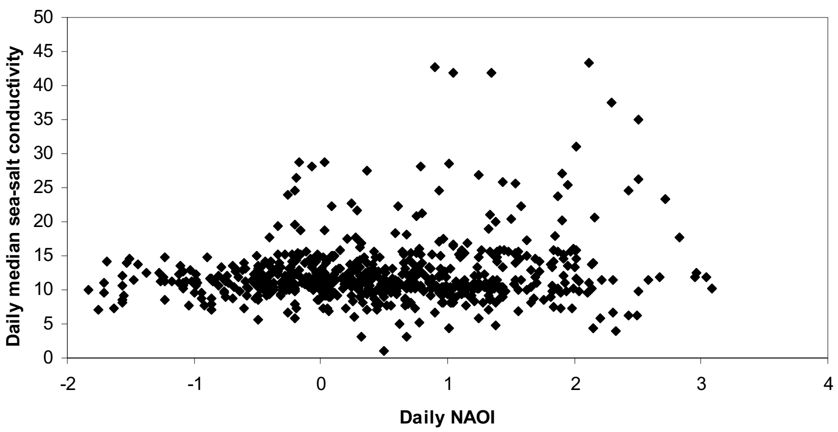

Fig. 10. *Correlation plot between daily median sea-salt conductivity, estimated from the sub-hourly dataset (in µS cm^{-1}) and the daily NAOI.*

differences reflect the complexity and the variability in time of the relationship between sea-salt conductivity and NAOI, which is manifested in time delays governed by atmospheric processes in addition to catchment processes.

Climatic patterns other than the NAOI may also influence the changes in sea-salt conductivity in the Allt a'Mharcaidh stream. For example, Middleton and Dixon (2001) observed that large positive NAOI values may be associated with strong Westerlies whilst small negative values may be associated with Easterlies.

Ness *et al*. (2004) found that, over recent years, the NAOI has tended towards a more positive phase and that it is expected to continue to increase over the next 100 years. More season-long positive NAOI would then lead to more sea-salt deposition, thus to more acid episodes. Estimation of acid episodes in the future, considering not only the NAOI but also other climatic patterns, has still to be fully investigated.

Conclusion

This paper has investigated the drivers that control the severity of acid episodes in upland catchments using sub-hourly monitored pH and EC data and illustrates the value

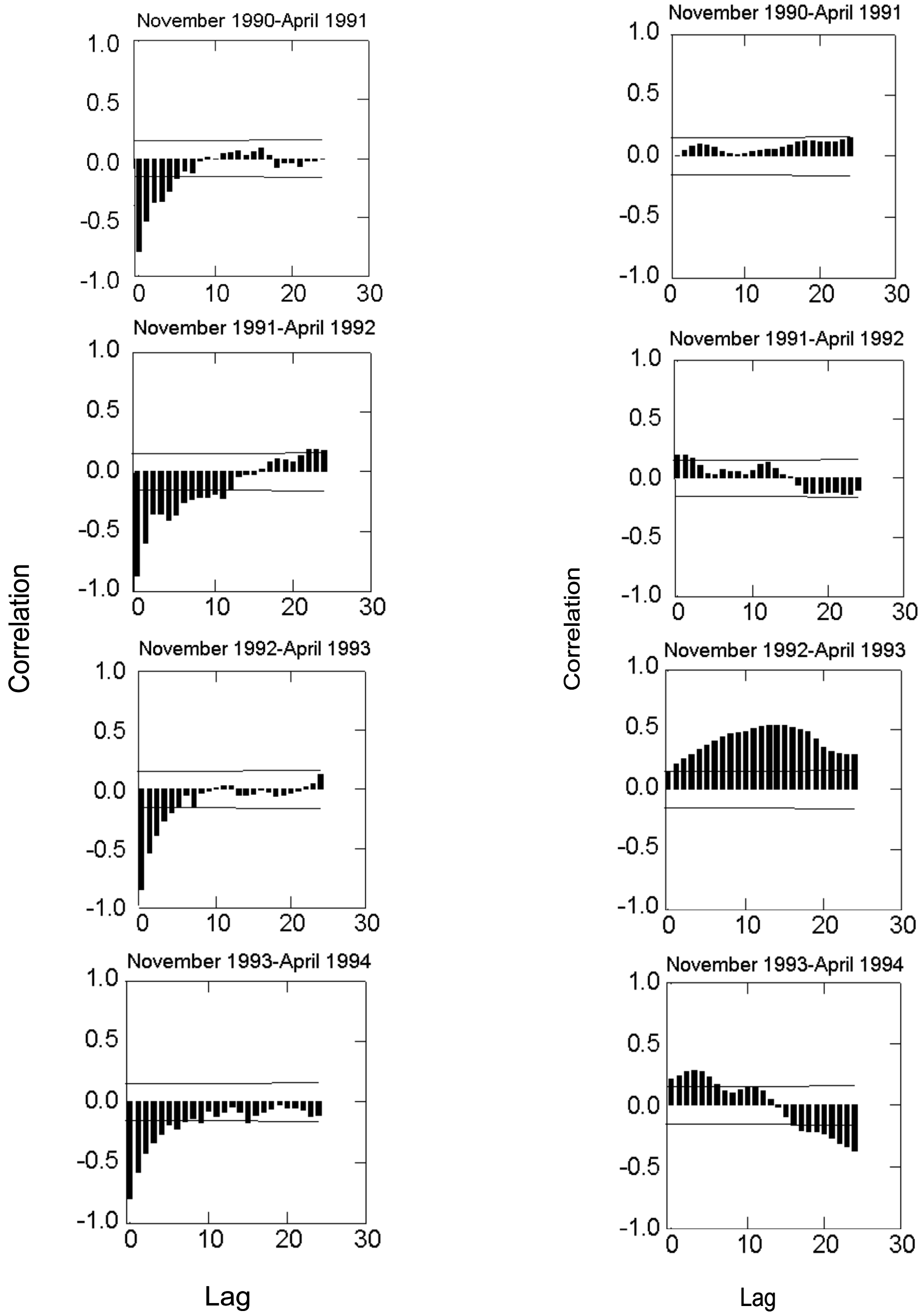

Fig. 11. *Left: Cross correlation functions for daily median pH and daily median flow (m^3 s^{-1}) for each of the 4 winter periods; Right: Cross correlation functions for daily median sea-salt conductivity (μS cm^{-1}) and daily NAOI for each of the 4 winter periods (for both figures, the dark horizontal lines represent the levels of significance for the cross-correlation between the 2 variables).*

of sub-hourly monitoring, rather than periodic spot sampled data, in providing more detailed indications about the processes that drive acidic episodes. Indeed, using weekly monitored data, not all episodes would have been picked up. Using high time-resolution data (i.e. sub-hourly frequency) enabled the identification of more episodes, thus revealing the different factors and processes triggering these events. It is, therefore, important to continue sub-hourly monitoring and to extend such monitoring to other sites.

For this Allt a'Mharcaidh case study, the sea-salt conductivity was found to be an important explanatory variable in terms of episode severity followed by the peak instantaneous flow rate and either the three-week ARI or the episode duration.

The multiple regression equations developed based on the data from 1991 to 1994, need to be tested on more recent or

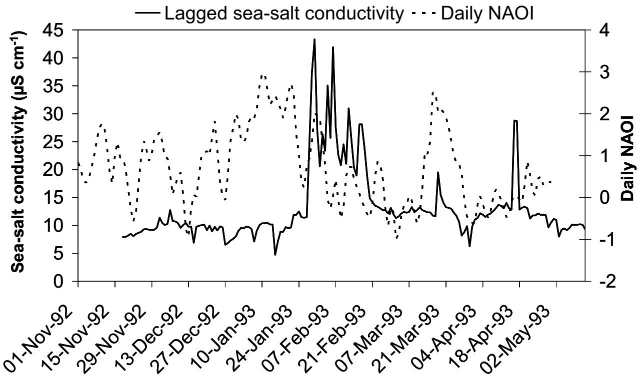

Fig. 12. *Time-series plot of sea-salt conductivity (µS cm^{-1}) and daily NAOI, with a time lag of 13 days between both time–series, for November 1992–May 1993.*

future data to establish whether the same controls of episode severity still operate. Indeed, perhaps one of the most valuable aspects of the use of the multiple regressions is as an 'exploratory tool' for examining when the model would or would not fit the observations. Thus, deviations from a good fit could provide clues to identify whether drivers other than those considered here should be considered in the model or whether inappropriate solutions for current drivers such as climate change have been chosen.

Following up on the importance of sea-salt conductivity, the first steps to correlate climate change indicators such as the NAOI and the runoff chemistry for upland sites have been undertaken. This opens the way to extend the study to other climate indicators (e.g. Lamb Weather Types) and other sites, thus facilitating the developments of relationships that would enable the inclusion of climate change in catchment-based models such as MAGIC (Cosby *et al*., 1985; Evans, 2004). However, to consider longer term changes and to pin down more fully the critical atmospheric patterns, high quality, long-term datasets are required, as are field measurements with quality control checks.

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